



# Complexes of the Group 5 Elements

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## 2.1 General Remarks

Paddlewheel compounds having two dimetal units, each with a square planar configuration, and each group parallel to the other are relatively new in group 5. With other transition metal atoms, this type of atom arrangement is commonly found for  $M_2^{n+}$  units where  $n = 4, 5$  or  $6$ . This means that the oxidation state for each metal atom is between 2 and 3. It has been generally thought that when the formal oxidation numbers are higher the atoms shrink so much that good orbital overlap necessary for metal–metal bond formation is not attained. Oxidation numbers of less than two are not common in inorganic compounds of the first transition series, with the exception of Cu or when compounds are stabilized by  $\pi$ -donors such as carbonyl groups which are not generally covered in this monograph. Therefore only a few examples of compounds with values of  $n$  outside the range 4–6 are known. For the group 5 elements, compounds in which the metal atom has an oxidation number of three are commonly found forming edge-sharing bioctahedra, not paddlewheel compounds. Lower oxidation numbers such as two give rise to only a few coordination complexes for vanadium; an even lesser number is known for niobium and tantalum. Therefore part of the challenge in synthesizing metal–metal bonded paddlewheel compounds of the group 5 elements is the development of appropriate synthetic procedures that produce precursors in low oxidation states. Most of the compounds of the paddlewheel type for vanadium and niobium have the metal atom in the divalent state in a  $d^3$  electronic configuration. The overlap of these  $d^3$ – $d^3$  atoms give triply bonded dimetal units with an expected electronic configuration of  $\sigma^2\pi^4$  or a variation thereof.

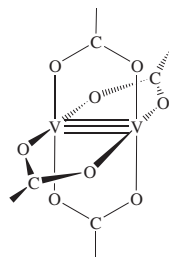
## 2.2 Divanadium Compounds

Theoretical calculations at the Fenske-Hall and Hartree-Fock level for the model system  $V_2(O_2CH)_4$ , which had been carried out in the mid-eighties, indicate that multiple bonds between vanadium atoms should be stable.<sup>1</sup> The calculations clearly show the possible existence of paddlewheel molecules of the type 2.1 and predict a vanadium-to-vanadium triple bond length between 2.0 and 2.1 Å with a  $\sigma^2\pi^4$  electronic configuration for the  $V_2^{4+}$  unit. However, all efforts to synthesize  $V_2(\text{carboxylato})_4$  compounds from the reaction of carboxylates and a few known  $V^{2+}$  starting materials available<sup>2</sup> (e.g.,  $V(H_2O)_6(CF_3SO_3)_2$ ,  $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$  or  $VCl_2(py)_4$ ) fail to produce dinuclear complexes.<sup>3</sup> These reactions give oxo-centered trinuclear

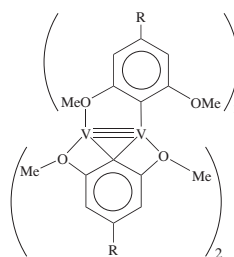
species of the type  $[V_3(\mu_3-O)(\text{carboxylato})_6L_3]^{n+}$ , where  $n = 0, 1$  and  $L =$  a neutral donor molecule such as  $H_2O$ , THF or py.

Likewise, early attempts at reacting formamidinates with divalent starting materials such as  $VCl_2(py)_4$  gave only mononuclear compounds. An example is *trans*- $V(py)_2(DTolF)_2$  which is made by reacting *trans*- $VCl_2(py)_4$  with LiDTolF, DTolF = *N,N'*-di-*p*-tolylformamidinate.<sup>4</sup>

A triple bond between vanadium atoms has been claimed for two compounds of the type 2.2 for  $R = H^5$  and  $OCH_3^6$  which have V–V distances of 2.200(2) and 2.223(2) Å, respectively. However, these compounds are better described as edge-sharing bioctahedra (ESBO), not paddlewheel compounds. A reaction of *trans*-(tmeda) $_2VCl_2$  (tmeda = tetramethylethylenediamine) and the amidate salt, Na(PhNC(CH<sub>3</sub>)O) gives another ESBO compound but without metal–metal bonding. This is  $\{[PhNC(CH_3)O]_4V\}_2(tmeda)$ .<sup>7</sup>



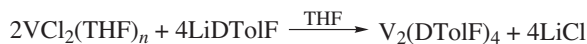
2.1



2.2

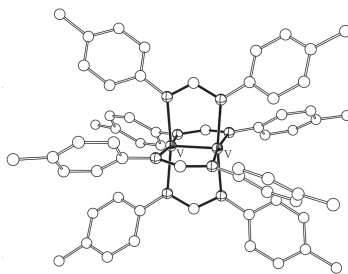
### 2.2.1 Triply-bonded divanadium compounds

The first paddlewheel compound containing the triply-bonded  $V_2^{4+}$  core was prepared after a systematic study of the chemistry of  $V^{2+}$ . The key step in the synthesis is the use of a THF solution of  $VCl_3(THF)_3$  which is reduced with one equivalent of  $NaEt_3BH$ . The reddish-purple solution of  $VCl_2(THF)_n$  reacts with LiDTolF to produce the air-sensitive, diamagnetic compound  $V_2(DTolF)_4$  in yields as high as 90%.<sup>8</sup>



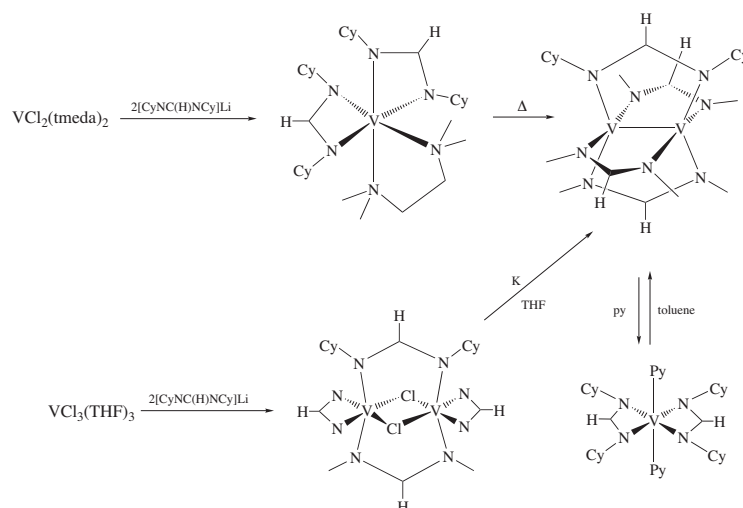
Crystals from toluene solutions layered with hexanes at  $-70^\circ C$  produce  $V_2(DTolF)_4 \cdot \text{toluene}$  which belong to a tetragonal system. The compound has a short V–V distance of 1.978(2) Å and the structure shown in Fig. 2.1.<sup>8</sup> This structure is of the same type as other dinuclear formamidinato complexes having four bridging ligands and it is homologous to that of the dimolybdenum and ditungsten complexes mentioned in Chapters 4 and 5, respectively. When crystallization is carried out at  $-70^\circ C$  from solutions of the compound in neat toluene, an orthorhombic form with a V–V distance of 1.974(4) Å is obtained.<sup>9</sup>

The  $V_2(DTolF)_4$  molecule is very stable in THF, toluene, and benzene solutions as long as they are protected from oxygen. In the presence of dry oxygen, they react to produce reddish orange  $V_2O_2(DTolF)_4$  and the corresponding greenish monomer  $VO(DTolF)_2$ .<sup>9</sup> In pyridine solution, the dinuclear  $V_2(DTolF)_4$  species is stable for short periods of time. An analysis of the  $^1H$  NMR spectra of the solid that remains after pyridine solutions are dried shows that the dinuclear unit remains intact after 1 h at room temperature. However, if the solutions are refluxed in neat pyridine, the color rapidly changes from red to purple due to the formation of *trans*- $V(py)_2(DTolF)_2$ .



**Fig. 2.1.** The paddlewheel molecule in the tetragonal form of  $V_2(DTolF)_4 \cdot \text{toluene}$ .

The method of preparation of  $V_2(DTolF)_4$  has been shown to be very useful for the synthesis of other triply-bonded divanadium compounds with a variety of formamidinate, aminopyridinate and guanidinate ligands.<sup>10,11</sup> However, special precautions must be taken when reacting ligands with electron-withdrawing substituents that disfavor the formation of vanadium–vanadium bonds. Thus, for  $N,N'$ -di-*p*-chlorophenylformamidinate ( $D^ClPhF$ ), reaction time must be limited to 15 min to avoid formation of oily substances.<sup>10</sup> Less basic formamidinates such as  $N,N'$ -di-2,5-chlorophenylformamidinate do not produce dinuclear compounds and only the corresponding tris-chelated mononuclear complex  $Li(THF)_4[V(\text{form-amidinate})_3]$  can be isolated. Attempts to carry out the reaction at higher temperatures led to cleavage of the formamidinate groups.<sup>10</sup> An alternative method of synthesis of V–V bonded compounds begins with the reaction of *trans*- $VCl_2(\text{tmeda})_2$ <sup>12,13</sup> and  $LiDCyF$  ( $DCyF = N,N'$ -dicyclohexylformamidinate) in toluene at room temperature. This produces the mononuclear compound  $V(\text{tmeda})(DCyF)_2$  which upon heating gives dinuclear  $V_2(DCyF)_4$  with a V–V distance of 1.968(2) Å. This compound, like  $V_2(DTolF)_4$ , reacts with pyridine to give the mononuclear complex *trans*- $V(\text{py})_2(DCyF)_2$  which in turn reverts to the dinuclear species in refluxing toluene.<sup>13</sup> An alternative route to  $V_2(DCyF)_4$  is reaction of  $VCl_3(THF)_3$  with  $LiDCyF$  to produce  $(\eta^2\text{-DCyF})V(\mu\text{-Cl})_2(\mu\text{-DCyF})_2V(\eta^2\text{-DCyF})$  which can be reduced in THF by potassium metal.<sup>13</sup> These reactions are summarized in the chart:



All compounds that have been structurally characterized are listed in Table 2.1. Compounds with a  $V_2^{4+}$  core are diamagnetic and have the typical paddlewheel structure, Fig. 2.1, with

V–V bond distances ranging from 1.932(1) Å for  $V_2(\text{hpp})_4$  to 1.988(1) Å for  $V_2(\text{DAniF})_4$ , where hpp is the anion of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine, 2,3, and DAniF is *N,N'*-di-*p*-anisylformamidinato. The longer distances correspond to the formamidinates, while the shorter ones belong to compounds with more basic aminopyridinate (ap) and guanidinate ligands, e.g., hpp and 1,2,3-triphenylguanidinate (TPG). The later is shown in Fig. 2.2. It should be noted that the V–V bonds are the only metal–metal bonds, other than the so-called supershort Cr–Cr quadruple bonds, that are shorter than 2.0 Å. The formal shortness ratio, FSR (see Section 3.2.1), which is a measure of the bond shortness normalized to atomic size, range from 0.790 for  $V_2(\text{hpp})_4$  to 0.812 for  $V_2(\text{DAniF})_4$ . These FSRs are similar to those for the supershort Cr<sub>2</sub> bonds, the smallest of which is 0.770 for Cr<sub>2</sub>(2-MeO-5-MeC<sub>6</sub>H<sub>4</sub>).

**Table 2.1.** Structural data for divanadium paddlewheel compounds

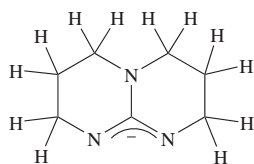
Compound	$r(\text{V}-\text{V})^a$ (Å)	core	ref.
$V_2(\text{hpp})_4$	1.932(1)	$V_2^{4+}$	11
$V_2(\text{ap})_4 \cdot 2C_6H_6$	1.942(1)	$V_2^{4+}$	10
$V_2(\text{TPG})_4 \cdot 4C_6H_6$	1.952(1)	$V_2^{4+}$	10
$V_2(\text{DCyF})_4$	1.968(2)	$V_2^{4+}$	12,13
$V_2(\text{DTolF})_4 \cdot C_7H_8^b$	1.978(2)	$V_2^{4+}$	8,9
$V_2(\text{DTolF})_4 \cdot C_7H_8^c$	1.974(4)	$V_2^{4+}$	9
$V_2(\text{D}^{\text{Cl}}\text{PhF})_4^d$	1.974(1)	$V_2^{4+}$	10
	1.982(1)		
$V_2(\text{DPhF})_4^d$	1.978(1)	$V_2^{4+}$	10
	1.979(1)		
$V_2(\text{DAniF})_4$	1.988(1)	$V_2^{4+}$	10
$K_3(\text{THF})_3[V_2(\text{DPhF})_4]$	1.929(1)	$V_2^{3+}$	10,15
$[K(18\text{-crown-6})(\text{THF})_2][V_2(\text{DPhF})_4]$	1.924(2)	$V_2^{3+}$	10

<sup>a</sup> Distances are given with up to 3 decimal digits.

<sup>b</sup> Tetragonal form.

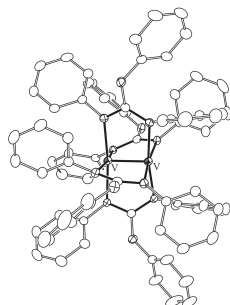
<sup>c</sup> Orthorhombic form.

<sup>d</sup> Two independent molecules.



### 2.3

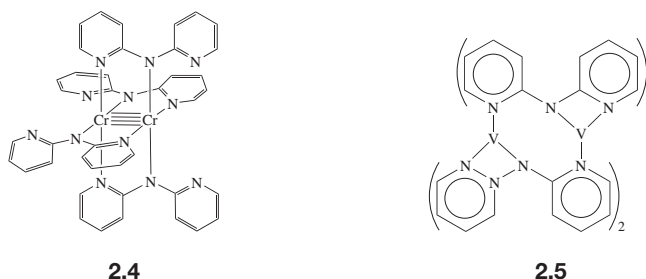
The electrochemistry of some of  $V_2^{4+}$  species has been studied. While no reversible oxidation occurs, the cyclic voltammograms in THF solutions containing 0.1 M  $\text{Bu}_4\text{NPF}_6$  and using Ag/AgCl reference electrodes show a reversible wave at negative potentials. The reduction wave appears at an  $E_{1/2}$  of -1.23, -1.46, -1.77, -1.82 and -1.99 V for  $V_2(\text{D}^{\text{Cl}}\text{PhF})_4$ ,  $V_2(\text{DPhF})_4$ ,  $V_2(\text{DAniF})_4$ ,  $V_2(\text{ap})_4$  and  $V_2(\text{TPG})_4$ , respectively.<sup>10</sup> This shows that as the ligands become more basic the reduction is more difficult.



**Fig. 2.2.** The triply-bonded  $V_2^{4+}$  unit bridged by 1,2,3-triphenylguanidinate ligands in  $V_2(TPG)_4 \cdot 4C_6H_6$ .

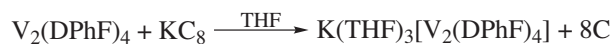
### 2.2.2 Metal–metal vs metal–ligand bonding

As mentioned above, the use of electron-withdrawing substituents in formamidinate ligands such in  $N,N'$ -di-3,5-chlorophenylformamidinate or  $N,N'$ -di-*p*-trifluoromethylformamidinate prevents the formation of V–V bonds and a tris-chelating species is favored.<sup>10</sup> Reaction of  $V_2(DTolF)_4$  and pyridine also gives six-coordinate mononuclear species.<sup>9</sup> Interestingly, reaction of  $VCl_2 \cdot nTHF$  with the anion of 2,2'-dipyridylamine (dpa) which is well known to form compounds such as 2.4 having metal-metal bonds, fails to produce V–V bonds in 2.5 which have two six-coordinate vanadium species.<sup>14</sup> The difference between these two types of compounds is that in 2.5 the four groups that were dangling in 2.4 form two bonds to each metal atom and the M–M bond disappears. This indicates that there is a fine line between the formation of the metal–metal bond and the metal–ligand bonds.



### 2.2.3 Divanadium compounds with the highly reduced $V_2^{3+}$ core

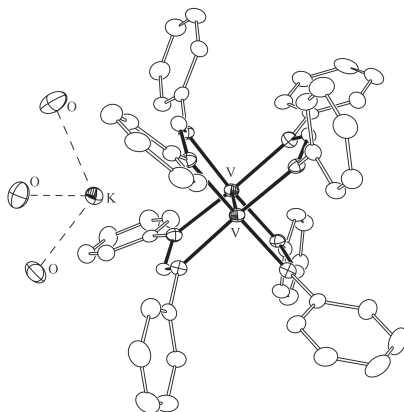
Chemical reduction of  $V_2(DPhF)_4$  with potassium graphite in THF allows the isolation of the first four-bladed paddlewheel complex with a  $V_2^{3+}$  core in  $K(THF)_3[V_2(DPhF)_4]$ .<sup>15</sup> During the reaction, which proceeds according to



the red-brown, diamagnetic  $V_2^{4+}$  complex is transformed to a dark-green, paramagnetic complex with a  $V_2^{3+}$  core. The compound is extremely air-sensitive and must be crystallized quickly at temperatures below  $-10^\circ C$ . Otherwise it reverts to the triply-bonded diamagnetic species. An X-ray study reveals that the paddlewheel structure is conserved but the V–V bond contracts significantly to a distance of  $1.929(1) \text{ \AA}$ , a difference of  $0.05 \text{ \AA}$  when compared to the neutral species.<sup>15,10</sup> The shortening of this bond is due the increase of bond order from 3 to 3.5 upon

addition of an electron. The magnitude of the change, which is similar to that obtained upon oxidation of  $\text{Mo}_2(\text{carboxylato})_4$  compounds discussed in Chapter 4, suggests that the additional electron resides in the  $\delta$ -orbital and that the dimetal core has a  $\sigma^2\pi^4\delta$  configuration. The average V–N distance increases from 2.101[3] to 2.142[3] Å upon reduction.

As shown in Fig. 2.3, the  $\text{K}^+$  cation is found in one of the pockets between two of the formamidinate ligands but the distances to the N atoms of over 3.0 Å are too long to be considered of chemical importance. This type of association of an alkali metal cation with some ligands of an  $\text{M}_2$  paddlewheel molecule has been observed also in  $\text{Nb}_2(\text{hpp})_4$  (Section 2.3.1) and  $\text{W}_2(\text{hpp})_4$  (Chapter 5) and creates a few minor distortions to the angles between paddles.



**Fig. 2.3.** The structure of  $\text{K}(\text{THF})_3[\text{V}_2(\text{DPhF})_4]$  that has a highly reduced  $\text{V}_2^{3+}$  core showing the position of the potassium ions between the paddles of the anion.

The potassium cation can be easily removed from the pocket by addition of a crown ether.<sup>10</sup> This gives the more stable complex  $[\text{K}(18\text{-crown-6})(\text{THF})_2][[\text{V}_2(\text{DPhF})_4]]$  which does not revert to the  $\text{V}_2^{4+}$  species as long as it is protected from oxygen. The V–V distance of 1.924(2) Å is the same within  $3\sigma$  to that in  $\text{K}(\text{THF})_3[\text{V}_2(\text{DPhF})_4]$  (1.929(1) Å). This supports the notion that the presence or absence of the alkali metals in the pockets between paddles does not alter the metal–metal interaction.

Although the reduced species can be formally considered to provide an example of a rare monovalent oxidation state for the vanadium atom, this is not the best view as the additional electron is introduced into the  $\delta$  bonding orbital, where it is delocalized on the  $\text{V}_2^{3+}$  core. This is supported by EPR results. A frozen THF solution of  $\text{K}(\text{THF})_3[\text{V}_2(\text{DPhF})_4]$  at 6 K gave a 15-line spectrum which indicates that the electron is coupled to each  $^{51}\text{V}$  ( $I = 7/2$ ) atom equally. A simulation of the main feature gives a  $g$  value of 1.9999. Although this value is close to the free-electron value, the complicated hyperfine splitting pattern indicates that the unpaired electron is localized on the metal core.<sup>10,15</sup>

These are the first structurally characterized compounds with an  $\text{M}_2^{3+}$  core in a tetragonal paddlewheel environment. There are only four other compounds known to contain such core but they are in a trigonal paddlewheel environment (with only three bridging ligands, not four bridging groups). In the latter,  $\text{M} = \text{Fe}$  and  $\text{Co}$  and they are discussed in Sections 11.2 and 11.3.2, respectively. A compound that has been isolated in the solid state and presumed to have a  $\text{Co}_2^{3+}$  core bridged by four benzamidinate ligands is mentioned in Section 11.3.1.

### 2.3 Diniobium Compounds

Divalent compounds of niobium can be classified as mononuclear, polynuclear and organometallic.<sup>16</sup> Paramagnetic, octahedral  $\text{NbX}_2\text{L}_4$ ,  $\text{X} = \text{Cl}$  and  $\text{L} = \text{PMe}_3$ ,  $1/2\text{dmpe}$ <sup>17</sup> or  $\text{X} = \text{OAr}$  and  $\text{L} = 1/2\text{dmpe}$ <sup>18</sup> are prepared by reduction of higher oxidation state niobium chlorides or aryloxides with sodium amalgam. Potassium graphite,  $\text{KC}_8$ , works best for the reduction of  $\text{NbCl}_4(\text{THF})_2$  in pyridine in the preparation of *trans*- $\text{NbCl}_2(\text{py})_4$ .<sup>19</sup> A few anionic species of the type  $[\text{Nb}_2\text{Cl}_6(\text{THT})_3]^{2-}$  and  $[\text{Nb}_2\text{Cl}_5(\text{THT})(\text{py})_3]$  are also known.<sup>20</sup> In these face-sharing bioctahedral (FSBO) complexes there are formal triple bonds between the metal atoms, but the Nb–Nb distances of *c.* 2.6 Å are rather long. These FSBO compounds are not covered in this monograph which is devoted to paddlewheel and some related complexes. The M–M distances in paddlewheel compounds are given in Table 2.2.

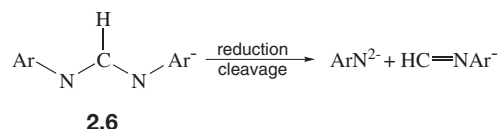
**Table 2.2.** Structural data for diniobium compounds

Compound	$r(\text{Nb-Nb})^a$ (Å)	core	ref.
$\text{Nb}_2(\text{hpp})_4$	2.204(1)	$\text{Nb}_2^{4+}$	22,23
$\text{Nb}_2(\text{hpp})_4 \cdot \text{Na}(\text{C}_2\text{H}_5)_3\text{BH}$	2.219(1)	$\text{Nb}_2^{4+}$	23
$\text{Nb}_2(\text{hpp})_4 \cdot 2\text{Na}(\text{C}_2\text{H}_5)_3\text{BH}$	2.206(1)	$\text{Nb}_2^{4+}$	23
$\text{Nb}_2(\text{azin})_4 \cdot 2\text{LiCl} \cdot 4\text{THF}$	2.278(2)	$\text{Nb}_2^{4+}$	23
$\text{Nb}_2(\text{azin})_4 \cdot 4\text{THF}$	2.263(1)	$\text{Nb}_2^{4+}$	25
$\text{Nb}_2(\text{azin})_4 \cdot 2\text{LiCl} \cdot 6\text{THF}$	2.268(1)	$\text{Nb}_2^{4+}$	26
$\text{Na}_4\text{Nb}_2(\text{calix})_2 \cdot 10\text{C}_4\text{H}_8\text{O}_2$	2.385(2)	$\text{Nb}_2^{4+}$	28

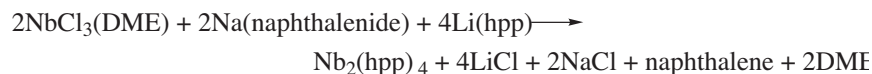
<sup>a</sup> Distances are given with up to 3 decimal digits.

#### 2.3.1 Diniobium paddlewheel complexes

Early attempts at preparing paddlewheel complexes having diniobium or ditantalum units analogous to  $\text{V}_2(\text{formamidinato})_4$  were stymied not only by the lack of divalent species that could be used as starting materials but mainly by another severe difficulty: under the reaction conditions necessary to reduce the precursor to the divalent state, ligands such as formamidinates, 2.6, readily cleave.<sup>21</sup>



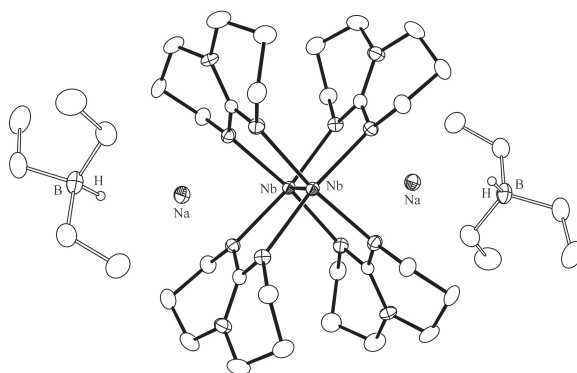
To avoid the cleavage of the ligands, the more robust guanidinate hpp ligand 2.3 was the first to be used to prepare compounds of the paddlewheel type.<sup>22</sup> The hpp ligand is more resistant toward cleavage because of the support provided by other bonds within it. The compound  $\text{Nb}_2(\text{hpp})_4$  was made in 17% yield by reacting  $\text{NbCl}_3(\text{DME})$  with a mixture of  $\text{Lihpp}$  and  $\text{KC}_8$  in THF. The yield was improved to *c.* 47% when lithium naphthalenide was used as reducing agent instead of the less soluble  $\text{KC}_8$ .<sup>23</sup>



The green, air-sensitive compound is diamagnetic and has a centrosymmetric structure with the four hpp ligands forming bridges between two niobium atoms at a distance of 2.204(1) Å.<sup>22</sup>

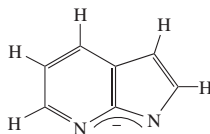
This Nb–Nb distance is shorter by *c.* 0.4 Å than the corresponding distances in FSBO compounds mentioned earlier but it is 0.27 Å longer than that found in the isostructural vanadium complex cited in Section 2.2.1. Also, it is significantly shorter than that in niobium itself (2.85 Å) which is one of the most refractory metals (mp 2468 °C). The diamagnetic nature of the compound and the short Nb–Nb distance are consistent with an electronic structure of the type  $\sigma^2\pi^4$  with no unpaired electrons. The structure was predicted (genuinely, before the compound was made) by density functional theory.<sup>24</sup> The calculated Nb–Nb distance is 2.225 Å for the model compound  $\text{Nb}_2(\text{HNCHNH})_4$  and the calculated Nb–N distance is 2.20 Å which is the same in  $\text{Nb}_2(\text{hpp})_4$ .

When  $\text{Nb}_2(\text{hpp})_4$  is placed in contact with  $\text{NaEt}_3\text{BH}$ , the solubility properties change dramatically. While  $\text{Nb}_2(\text{hpp})_4$  is relatively insoluble in THF but soluble in toluene, a new species is formed which is soluble in THF but insoluble in toluene. Crystallization of mixtures of these reagents provide crystals of  $\text{Nb}_2(\text{hpp})_4\cdot\text{NaEt}_3\text{BH}$  and  $\text{Nb}_2(\text{hpp})_4\cdot 2\text{NaEt}_3\text{BH}$ . In these compounds, the sodium atoms are between paddles of the paddlewheel structure as shown in Fig. 2.4 for  $\text{Nb}_2(\text{hpp})_4\cdot 2\text{NaEt}_3\text{BH}$ .<sup>23</sup> Even though there are small deviations in the N–Nb–N angles relative to those of  $\text{Nb}_2(\text{hpp})_4$ , the Nb–Nb distances are essentially unchanged (see Table 2.2). These are 2.206(1) and 2.219(1) Å for  $\text{Nb}_2(\text{hpp})_4\cdot 2\text{NaEt}_3\text{BH}$  and  $\text{Nb}_2(\text{hpp})_4\cdot\text{NaEt}_3\text{BH}$ , respectively.



**Fig. 2.4.** The structure of  $\text{Nb}_2(\text{hpp})_4\cdot 2\text{NaEt}_3\text{BH}$  showing the puckering of the guanidinate ligand hpp and the position of the sodium cations between the clefts of the neutral, triply-bonded paddlewheel unit.

The generality of the synthetic method of preparation of paddlewheel compounds with ligands protected from possible cleavage is shown by using the lithium salt of 7-azaindole,  $\text{Li}(\text{azin})$  (2.7) in place of  $\text{Lihpp}$ :



**2.7**

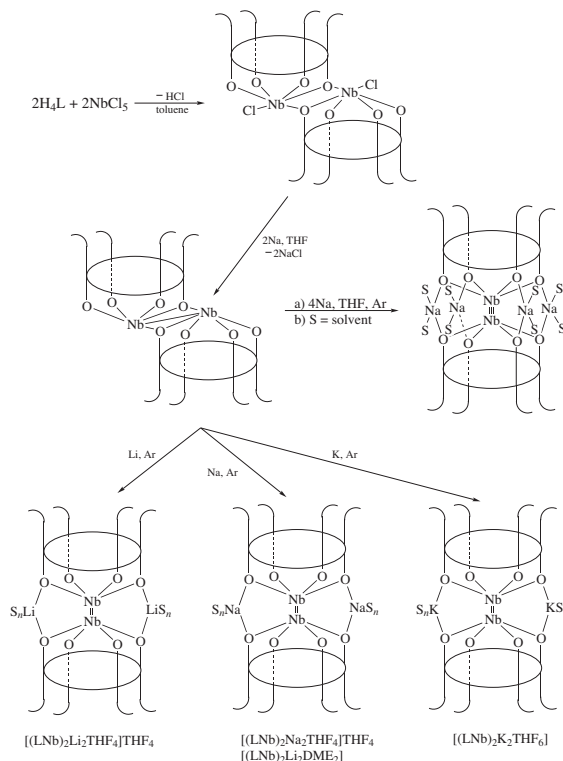
From THF solutions, crystals of composition  $\text{Nb}_2(\text{azin})_4\cdot 2\text{LiCl}\cdot 4\text{THF}$  are obtained.<sup>23</sup> The structure consists of two niobium atoms spanned by four azin ligands giving a Nb–Nb distance of 2.278(2) Å. There are also some very weak interactions with axial chloride ions. The Nb...Cl separation is 2.849(3) Å. Thus it is unlikely that the lengthening of *c.* 0.07 Å of the

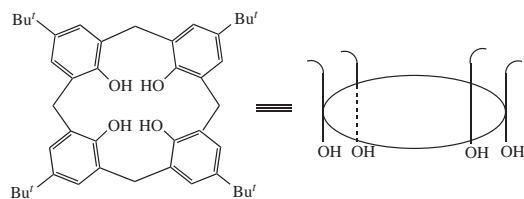
Nb–Nb distance relative to that in  $\text{Nb}_2(\text{hpp})_4$  is due to such interactions. This is more likely due to the geometrical character of the azin ligand which imposes a wider bite. The compound has been shown to be diamagnetic by the NMR spectrum.

There are two additional compounds having a  $\text{Nb}_2^{4+}$  core and four bridging azin groups. One was obtained by reaction of  $\text{Li}(\text{TMEDA})\text{Nb}_2\text{Cl}_5$  with 4 equiv of potassium 7-azaindolyl which affords  $\text{Nb}_2(\text{azin})_4 \cdot 2\text{THF}$ . This is described as red-orange and diamagnetic with a Nb–Nb distance of  $2.263(1) \text{ \AA}$ .<sup>25</sup> This compound does not have any chemically significant axial interactions. The other compound was made similarly by using the lithium salt of 7-azaindole. The compound, described as blue, has the formula  $\text{Nb}_2(\text{azin})_4 \cdot 2\text{LiCl} \cdot 6\text{THF}$ . The structure is similar to those described above and the Nb–Nb distance of  $2.268(1) \text{ \AA}$  is essentially unchanged but this compound like  $\text{Nb}_2(\text{azin})_4 \cdot 2\text{LiCl} \cdot 4\text{THF}$  has very weak Nb...Cl interactions with the corresponding distance being  $2.733(2) \text{ \AA}$ .<sup>26</sup> The odd thing about this compound is that it is described as being paramagnetic with a  $\mu_{\text{eff}}$  at room temperature that corresponds to *one* unpaired electron. This value drops to *c.*  $0.6 \mu_{\text{B}}$  at very low temperatures (nearly 0 K). This is in sharp contrast with the other two azin compounds which are diamagnetic and give very good  $^1\text{H}$  NMR data.

### 2.3.2 Diniobium compounds with calix[4]arene ligands and related species

There is a series of compounds which have  $\text{Nb}_2^{n+}$  units,  $n = 4, 6$ , and  $8$ , which correspond to formal bond orders of 3, 2 and 1, respectively.<sup>27–30</sup> Some reactions that lead to these compounds have been summarized<sup>31</sup> and are presented in the following scheme where the bond orders are shown by the number of lines between Nb atoms. The calix[4]arene,  $\text{H}_4\text{L}$ , that is typically employed is the *p-tert*-butyl derivative shown as **2.8** and the solvent *S* can be dioxane, diglyme or THF.

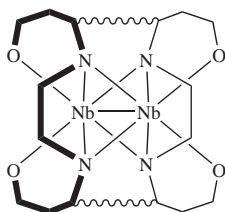




2.8

Many of these diamagnetic compounds have been characterized by X-ray crystallography. The Nb–Nb distances vary accordingly to the bond order. For example, the Nb–Nb singly-bonded compounds have distances of about 2.75 Å,<sup>28</sup> the doubly bonded Nb–Nb compounds have distances of *c.* 2.65 Å,<sup>30</sup> while those with Nb–Nb triple bonds have distances of *c.* 2.38 Å.<sup>28</sup> The latter is slightly longer than those in Nb<sub>2</sub> triply-bonded, paddlewheel complexes (see Table 2.2).

Another series of compounds with formal Nb–Nb bonds are those obtained by reductive coupling of Nb(Bu<sup>t</sup>-salophen)Cl<sub>3</sub>, where Bu<sup>t</sup>-salophen is *N,N'*-*o*-phenylenebis(salicylideneamine), which forms dinuclear compounds with C–C bonds across two imino groups of the ligand to give the Nb–Nb singly bonded compound Nb<sub>2</sub>(Bu<sup>t</sup>-\*salophen<sub>2</sub>\*), 2.9, where Bu<sup>t</sup>-\*salophen<sub>2</sub>\* represents a coupled salophen ligand.<sup>32</sup> This has a Nb–Nb bond distance of 2.653(1) Å. This can be reduced further by potassium to a transient compound that contains a Nb–Nb double bond.



2.9

## 2.4 Tantalum

As for niobium, there are only a few compounds with divalent tantalum atoms. Examples are the mononuclear TaCl<sub>2</sub>L<sub>4</sub>, L = PMe<sub>3</sub>, <sup>1</sup>/<sub>2</sub>dmpe,<sup>16</sup> and the dinuclear FSBO complexes of the type [Ta<sub>2</sub>X<sub>6</sub>(THT)<sub>3</sub>]<sup>2-</sup>,<sup>20</sup> the latter have long Ta–Ta distances of *c.* 2.6 Å. The FSBO compounds are not covered here. There are also Ta–Ta bonds in some low-valent halides and oxides, an example being Na<sub>0.74</sub>Ta<sub>3</sub>O<sub>6</sub><sup>33</sup> which is isomorphous with NaNb<sub>3</sub>O<sub>5</sub>F.<sup>34</sup> The metal–metal bond distance in Na<sub>0.74</sub>Ta<sub>3</sub>O<sub>6</sub> is 2.673 Å.

A report of a compound containing unsupported Ta<sup>III</sup>–Ta<sup>III</sup> bonds has appeared.<sup>35</sup> However, this has been shown to be in error.<sup>36</sup> The correct formula is [(Cy<sub>2</sub>N)<sub>2</sub>ClTa(μ-H)]<sub>2</sub> (Cy = cyclohexyl) which has a Ta<sup>IV</sup>(μ-H)<sub>2</sub>Ta<sup>IV</sup> core. To date, there are no known paddlewheel compounds.

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